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EPR of Ce^{3+} in the Rb_2NaYF_6 single crystal

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ABSTRACT

The EPR spectrum of the Ce^{3+} ion in the crystal of the elpasolite type Rb_2NaYF_6 has been observed and studied at low temperatures ($T = 4.2 - 80$ K). It was established that the paramagnetic center Ce^{3+} has tetragonal symmetry confirming the experimental fact we reported recently that at low temperatures the Rb_2NaYF_6 crystal exists in the tetragonal phase, into which it transferred from the cubic phase as a result of the structural phase transition (PT). Parameters of the spin Hamiltonian of the tetragonal EPR spectrum were determined. A scheme of 4f energy levels of the Ce^{3+} ion in Rb_2NaYF_6 before and after PT was proposed from the theoretical interpretation of the observed g-factors and parameters of the crystal fields acting on it were determined.

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1. Introduction

A family of crystals with the structure of cryolite-elpasolite A_2BCX_6 (A^+, B^+, C^{3+} are mono- and trivalent metal cations, X is the halogen anion: F^-, Cl^-, Br^-) is one of attracting types of crystals. Such compounds doped with rare-earth elements are promising materials for the practical usage in scintillators for X-rays, broad-band tunable lasers etc. [1,2]. It is known that such crystals at room temperature have the cubic elpasolite structure with the space group O_h^5 [3,4]. It was established experimentally that many of them, e.g., Cs_2NaYF_6, Cs_2NaScF_6 etc. keep this structure to low temperatures. It was assumed in many works that the symmetry of the Rb_2NaYF_6 crystal also remains cubic in a wide temperature interval ($4.2 - 300$ K) [5–9]. However our study of paramagnetic defects in Rb_2NaYF_6 using electron paramagnetic resonance (EPR) and optical spectroscopy showed that a PT takes place in this crystal at the temperature of 150 K [10]. Signals of paramagnetic centers with tetragonal symmetry formed by Dy^{3+} and Yb^{3+} ions were recorded in EPR spectra at low temperatures. It was found in the study of optical spectra of Yb^{3+} ions that cubic (T_c) paramagnetic centers of Yb^{3+} ions transform into centers of tetragonal symmetry (T_{tet}) in the vicinity of the temperature of 150 K. Some luminescence lines were split indicating splitting of cubic quartet energy levels of Yb^{3+} ions by the crystal field (CF) of tetragonal symmetry. The interpretation of these results showed that T_{tet} is formed due to the rotations of octahedra YbF_6 around fourfold axes and slight distortions of their structure. Theoretical calculations performed in Refs. [10,11] made it possible to estimate the value of the rotation angle of octahedra and present the pattern of their distortions. Simultaneously and independent of us the authors [12] studied the undoped Rb_2NaYF_6 crystal by Raman spectroscopy and hydrostatic pressure, and established that the PT from the cubic into the disordered phase accompanied by the recovery of the soft mode occurs in it at $T = 154$ K.

In this work we present results of studying EPR in the Rb_2NaYF_6 crystal containing paramagnetic centers formed by Ce^{3+} ions. The presence of only one type of centers with tetragonal symmetry at low temperatures indicates that the Rb_2NaYF_6 crystal has tetragonal symmetry. The obtained results again confirm the fact established earlier that the studied crystal transfers from the cubic into the tetragonal phase with the temperature decrease. The location of energy levels of the $4f^1$ configuration of the Ce^{3+} ion in the Rb_2NaYF_6 crystal is proposed in the theoretical interpretation of the values of g-factors of the observed T_{tet}. The values of parameters of the crystal field (CF) acting on it are determined from this scheme

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